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# ABSTRACTION OF HALOGEN ATOMS BY METHYL RADICALS

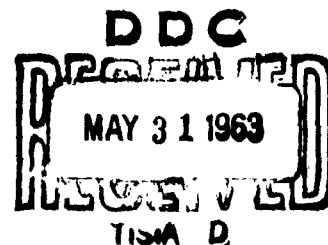
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Directorate of Materials and Processes  
Aeronautical Systems Division  
Air Force Systems Command  
Wright-Patterson Air Force Base, Ohio

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(Prepared under Contract No. AF 33(616)-7662 by Department  
of Chemistry, State University College of Forestry at  
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## FOREWORD

This report was prepared by Department of Chemistry, State University College of Forestry at Syracuse University, Syracuse 10, New York under USAF Contract AF 33(616)-7662. This contract was initiated under Project No. 7360, "The Chemistry and Physics of Materials," Task No. 736003, "Interaction of High Energy Forms with Materials." This work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with Mr. Denver Hale as project engineer.

This report covers work ending 30 October 1962.

## ABSTRACT

This report describes a study of halogen abstraction reactions described by the equation



in solution for  $R = CH_3, C_2H_5, iso-C_3H_7, t-C_4H_9, PhCH_2, CH_2Cl, CHCl_2, CCl_3$ , and  $CF_3$ . It was found that the Br abstraction from  $CCl_3Br$  proceeds about 1000 times faster than that from  $PhCH_2Br$  in spite of the fact that the respective C-Br bond dissociation energies are nearly equal. Similarly, the I abstraction from  $CF_3I$  was found to be about 500 times faster than that from  $CH_3I$ , although  $D(CH_3 - I)$  is again nearly equal to  $D(CF_3 - I)$ . These observations led to a notion that the repulsion between the approaching  $CH_3$  radical and the stretched C - X bond is an important factor in determining the rate of abstraction.

The ratios of  $k_2I/k_1$  and  $k_2, Br/k_1$  were found to be 45 and  $6 \times 10^{-3}$  respectively, and these rate constants are compared with  $k_2, H/k_1$ ;  $k_1$  being the rate constant of the reaction  $PhCH_3 + \cdot CH_3 \longrightarrow PhCH_2\cdot + CH_4$ .

The addition of  $CF_3$  radicals to propylene, isobutene, tetramethyl, ethylene, butadiene, cyclopentene, benzene, vinyl fluoride, vinyl chloride and 2-fluoropropylene have been investigated in the gaseous and liquid phases at  $65^\circ C$ . Some problems of cage recombination are discussed.

This technical documentary report has been reviewed and is approved.



RICHARD J. VOSELER, Capt, USAF  
Chief, Radiation Branch  
Physics Laboratory  
Directorate of Materials & Processes

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## Abstraction of Halogen Atoms by Methyl Radicals

### Part 1. Exchange Reactions Involving Methyl Iodide and Methyl Bromide

By F. W. Evans and M. Szwarc

Department of Chemistry, State University College of Forestry at  
Syracuse University, Syracuse 10, New York

The rate of halogen atom exchange was investigated in the following reactions:  $\text{CH}_3\text{I} + \cdot\text{CH}_3 \rightarrow \text{CH}_3 + \text{ICH}_3$  ( $k_2, \text{I}$ ) and  $\text{CH}_3\text{Br} + \cdot\text{CH}_3 \rightarrow \text{CH}_3 + \text{CH}_3\text{Br}$  ( $k_2, \text{Br}$ ). At 65°C the ratios  $k_2, \text{I}/k_1$  and  $k_2, \text{Br}/k_1$  were found to be 45 and  $6 \times 10^{-3}$  respectively,  $k_1$  being the rate constant of the reaction  $\text{Ph}\cdot\text{CH}_2 + \text{CH}_3 \rightarrow \text{PhCH}_2 + \text{CH}_3$ . The activation energies difference  $E_2, \text{I} - E_1$  was determined as -1.8 kcal/mole for the temperature range 55-85°C. The values of  $k_2, \text{I}/k_1$  and  $k_2, \text{Br}/k_1$  are compared with  $k_2, \text{H}/k_1$ . Although  $D(\text{CH}_3-\text{H}) = 102$  kcal/mole, thus being much greater than  $D(\text{CH}_3-\text{Br}) = 67$  kcal/mole, the rate constant  $k_2, \text{H}$  is only by a factor of 2-3 smaller than  $k_2, \text{Br}$ . The significance of this result is discussed.

Studies of the I exchange,  $\text{CH}_3\text{I} + \text{CH}_3 \rightarrow \text{CH}_3 + \text{ICH}_3$ , carried out in iso-octane solution led to a tentative suggestion that the iso-octyl radical may complex with methyl iodide.

### INTRODUCTION

Although much work has been carried out on metathetic reactions in which a hydrogen atom is abstracted from a suitable substrate by a radical or a free atom, hardly any kinetic work has been done on similar processes involving abstraction of halogen atoms. The published information about these reactions is mainly concerned with their synthetic aspects, as exemplified by the studies of Kharasch on  $\text{CCl}_4$  or  $\text{CCl}_3\text{Br}$  addition to olefins, or by similar investigations involving  $\text{CF}_3\text{I}$  which were explored thoroughly by Haszeldine. A comprehensive review of these processes is found in Walling's monograph *Free Radicals in Solution* (1957) where the reader may find numerous references to the original papers. The kinetics of halogen abstraction by polymeric radicals, i.e., chain-transfer reactions involving halogens, attracted some attention. For example, Gregg and Mayo<sup>1</sup> investigated the chain transfer constants to carbon tetrachloride, Fuhrman and Mesrobian<sup>2</sup> determined these constants to  $\text{CBr}_4$ , and Bamford and Dewar<sup>3</sup> studied the transfer reactions to some halogenated ethanes. These investigations suffer from the general difficulties common to any attempt of finding chain-transfer constants which result from the necessity of determining the number-average molecular weight of the product. Moreover, this method does not distinguish between different types of transfer, e.g., H-abstraction or Cl-abstraction and such an ambiguity is shown in the work of Bamford and Dewar.<sup>3</sup>

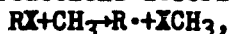
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Although studies of the chain-transfer reactions provide some fragmentary information on the kinetics of halogen abstraction, no attempt was made to investigate systematically the effect of the substrate's structure on the rate of these processes. The only systematic studies in this field were those of Polanyi and his co-workers who investigated the reaction,



where X denotes a halogen atom. The sodium-flame technique was developed for this purpose, and the available data were reviewed in 1951 by Warhurst.<sup>4</sup> However, sodium-flame reactions have specific features which distinguish them from similar radical reactions, and therefore there is need for a systematic study of halogen abstraction by other radicals or atoms.

This paper and the one immediately following report our first attempts to study systematically the reactions described by the equation,



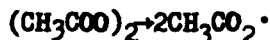
where X again denotes a halogen atom. The present communication deals with exchange reactions  $CH_3I + CH_3 \cdot \rightleftharpoons CH_3 \cdot + ICH_3$  and  $CH_3Br + CH_3 \cdot \rightleftharpoons CH_3 \cdot + BrCH_3$ , whereas in the second paper we consider the reactions of other halogen derivatives, namely those for which  $R = C_2H_5$ ,  $iso-C_3H_7$ ,  $t-C_4H_9$ ,  $Ph.CH_2$ ,  $CH_2Cl$ ,  $CHCl_2$ ,  $CCl_3$  and  $CF_3$ . The reactions reported in these two papers were carried out in solution, but we hope to discuss in a future publication the course of the same reactions taking place in the gas phase. Studies of halogen abstractions from other substrates are also under way in our laboratory.

#### Studies of Exchange Reactions Involving Methyl Radicals

Investigation of an exchange reaction requires labelling, and in this study  $Cl^{14}$  was used for this purpose. The kinetics of the exchange reaction  $CH_3I + CH_3 \cdot \rightleftharpoons CH_3 \cdot + ICH_3$  was investigated by two techniques, namely, (1) by reacting  $Cl^{14}H_3I$  with non-labelled methyl radicals and (2) by reacting  $Cl^{14}H_3$  with non-labelled methyl iodide. Only the first technique was feasible in studying the exchange  $CH_3Br + CH_3 \cdot \rightleftharpoons CH_3 \cdot + BrCH_3$ .

Our experimental approach to the problem is based on a method developed in this laboratory for determining methyl affinities of various aromatic and olefinic substrates. This method and its experimental justifications were reported in previous communications.<sup>5-7</sup> Therefore, only a brief description of the fundamental principles of this technique is given; however, all those details which are characteristic of the present studies are stressed and fully reported.

Methyl radicals were generated by thermal decomposition of acetyl peroxide in dilute solution in hydrocarbon. Such decomposition proceeds according to the equations,



and



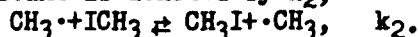
the decarboxylation of acetate radicals being an extremely rapid reaction. In fact, an independent study<sup>8</sup> has shown that under our experimental conditions the half-life time of acetate radicals is  $10^{-8}$ - $10^{-9}$  sec, and hence all the reactions taking place outside the "cage" are due to  $CH_3$  and not to  $CH_3COO$  radicals. This point was confirmed by independent investigations.<sup>9,10</sup> The "cage" reaction produces some ethane and methyl acetate;<sup>8</sup> however, as these processes do not affect our present studies, they need not be considered in this paper.

The conditions of our experiments were such that essentially all the methyl radicals which escaped from the "cage" reacted with solvent-producing methane and none with radicals present in the system.<sup>8</sup> If a substrate is added to the solution, then both the solvent and the substrate compete for methyl radicals. The ratio of the respective rate constants may therefore be determined from the outcome of such competitive experiments.

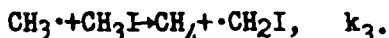
Let us now consider the situation created by addition of methyl iodide or methyl bromide to the peroxide solution. The reaction with solvent HS produces methane, and its rate constant is denoted by  $k_1$ , i.e.,



The reaction involving methyl iodide causes a reversible exchange of methyl radicals and its rate constant is denoted by  $k_2$ ,



Of course, methyl radicals may also react with methyl iodide according to reaction (3),



However, it will be shown that this last reaction is of no importance in the methyl iodide or methyl bromide system. In fact, in the following paper, a method will be discussed which permits us to determine  $k_3$  if its value is not much smaller than  $k_2$  or  $k_1$ ; and it is demonstrated that  $k_3$  is relatively large for such substrates as  $\text{CH}_2\text{ClBr}$  or  $\text{CHCl}_2\text{Br}$ , but negligible for  $\text{C}_2\text{H}_5\text{I}$  or  $\text{sec-C}_3\text{H}_7\text{I}$ .

The kinetic scheme discussed above implies that addition of methyl iodide or methyl bromide should not affect the yield of methane formed in the process. However, if  $\text{C}^{14}\text{H}_3\text{I}$  or  $\text{C}^{14}\text{H}_3\text{Br}$  is used in the experiment, the methane produced will acquire some radio-activity. Conversely, if  $\text{C}^{14}\text{H}_3$  radicals are generated from  $(\text{C}^{14}\text{H}_3.\text{COO})_2$ , then as a result of reaction (2), the specific activity of methane will be lower than that of methane formed in the absence of  $\text{CH}_3\text{I}$ . Hence, by determining the specific activity of methane formed in the presence of  $\text{CH}_3\text{I}$  (or  $\text{CH}_3\text{Br}$ ) and comparing it with that of methane produced in the absence of halide, we can calculate the ratio of  $k_2/k_1$  by the following procedure.

(1) In a reaction involving  $\text{C}^{14}\text{H}_3\text{I}$  (or  $\text{C}^{14}\text{H}_3\text{Br}$ ) and non-labelled methyl radicals, the amount of  $\text{CH}_3$  formed is very small compared with the amount of  $\text{CH}_3\text{X}$  present in the system. Hence, the specific activity of methyl halide remains constant during the exchange process, and the ratio  $k_2/k_1$  is given therefore by the equation

$$\frac{k_2}{k_1} = \frac{(\text{sp. act. CH}_4)}{(\text{sp. act. C}^{14}\text{H}_3\text{X}) - (\text{sp. act. CH}_4)} \frac{(\text{mole fraction of HS})}{(\text{mole fraction of C}^{14}\text{H}_3\text{X})}.$$

In applying this formula it is essential to ascertain that the total amount of  $\text{CH}_4$  formed in the process is not affected by the addition of  $\text{CH}_3\text{X}$  to the peroxide solution. If the specific activity of  $\text{CH}_4 \ll$  specific activity of  $\text{C}^{14}\text{H}_3\text{X}$  then

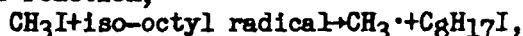
$$\frac{k_2}{k_1} = \frac{(\text{sp. act. CH}_4)}{(\text{sp. act. C}^{14}\text{H}_3\text{X})} \frac{(\text{mole fraction of HS})}{(\text{mole fraction of C}^{14}\text{H}_3\text{X})}.$$

(2) In a reaction involving a non-labelled methyl halide and  $C^{14}H_3$  radicals, we have to determine the total activity  $A_0$  of methane formed in the absence of methyl halide and the total activity  $A_f$  of the gas produced in the presence of methyl halide, no other change being made in the two otherwise identical experiments. It follows then that  $k_2/k_1 = \{(A_0 - A_f)/A_f\} \{(\text{mole fraction of HS})/(\text{mole fraction of } CH_3X)\}$ . Since the amount of  $CH_3X$  is much larger than the amount of  $CH_3$  produced, the reverse exchange process may be neglected.

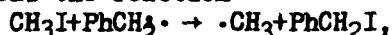
The convenient feature of the second method is that the derived formula applies also if the amount of methane formed increases on addition of the halide. It should be stressed that the total activity of  $CH_4$  is used in the second expression for the  $k_2/k_1$ , whereas the specific activity must be used in the first equation.

The problem of formation of additional amounts of methane, which arise from admixing methyl halide with peroxide solution, needs some clarification. In the proposed kinetic scheme, it has been assumed that methane results from reaction (1), that some methyl radicals exchange with methyl halide, and that none reacts with radicals ( $CH_3$  or others) present in the system. These assumptions are justified when the stationary concentration of  $CH_3$  radicals is sufficiently low, i.e., when the peroxide solution is very dilute and the temperature of the decomposition not too high. However, a further complication is possible. Reaction (1) produces solvent radicals S and these may react with methyl halide and generate more methyl radicals,  $CH_3X + S \rightarrow CH_3 + XS$ .

The occurrence of the last reaction increases, of course, the amount of methane formed in the process. It will be shown later that such a phenomenon was observed when iso-octane was used as a solvent. On the other hand, no additional methane was formed when the reaction was carried out in toluene. This means that the reaction,



is relatively fast, whereas the reaction



is extremely slow. Since the latter reaction is much more endothermic than the former, this observation is not surprising. In fact, the endothermicity of the benzyl radical reaction exceeds by about 10 kcal/mole that of the reaction involving iso-octyl radicals.

## Experimental

Procedure. The experimental procedure was essentially that described in detail in various publications from this laboratory (see e.g., ref. (5) and (7)). It consists in preparing deaerated solutions of acetyl peroxide with or without the investigated methyl halide, decomposing the peroxide at the desired temperature, and then determining the amounts of methane, ethane and carbon dioxide formed in the reaction. In addition, it was necessary to determine the radioactivity of the methane produced by the process. The counting was accomplished in Bernstein's proportional counting tubes in conjunction with an Atomic Instrument Co. proportional counter. The samples of methane were pumped into evacuated counting tubes by means of a Toepler pump. Thereafter, the tubes were filled with P-10 gas (90% A + 10%  $CH_4$ ) to a pressure of 1 atm, using for this purpose the filling device developed by Brookhaven National Laboratory. The activity of each sample was measured to 1% of statistical error at the middle of the "plateau" voltage. Background measurements were made before and after each determination,

the tube being first pumped out to  $10^{-5}$  mm Hg pressure, then refilled with P-10 gas and recounted by the standard procedure. The absolute activity of methane was determined by subtracting the background activity from the measured activity and correcting the resulting value for the dead volume of the counting tube.

For experiments involving  $\text{C}^{14}\text{H}_3$  radicals, no further calibration was necessary since the counting of the "blank" methane, i.e., of  $\text{CH}_4$  produced in the absence of methyl halide, provided the required data. In experiments which involved a radioactive methyl halide, determination of its specific activity was necessary. This was done by converting the methyl halide into methane via the Grignard compound and then counting the resulting gas as described above. The methane was passed through a liquid-nitrogen trap, to remove any trace of methyl halide, before being introduced into the counting tube. The results were checked by direct counting of the methyl halide, using for this purpose a Packard scintillation counter and the N.B.S. radioactive benzoic acid (in toluene solution) to determine the counting efficiency. A comparison of these two methods is shown in table 1.

Table I. Specific Activity of Methyl Bromide

Method	Dilution factor	Amount of diluted $\text{CH}_3\text{Br}$ $\mu\text{mole}$	Activity of diluted $\text{CH}_3\text{Br}$ c.p.m.	Spec. activity of original $\text{CH}_3\text{Br}$ c.p.m./ $\mu\text{mole}$
conversion to $\text{CH}_4$ ,	131.8	$7.53 \times 10^{-3}$	4062	$7.10 \times 10^7$
proportional counting	131.8	$10.82 \times 10^{-3}$	5935	$7.21 \times 10^7$
			average	$7.15 \times 10^7$
MeBr, scintillation counter	150.0	$26.6 \times 10^{-3}$	14,700	$8.3 \times 10^7$
	54.2	$310 \times 10^{-3}$	$1.04 \times 10^6$ (?)	$5.6 \times 10^7$ (?)

The result marked by a question mark is not reliable. The activity of the sample was too high and, therefore, its counting gave a too low value.

#### Materials

Iso-octane: Phillips Petroleum Co. Spectrograde; dried and purified by passing through a silica gel column.

Toluene: ACS-grade toluene, dried and purified as stated above.

Acetyl Peroxide: Prepared as described in ref. (7), p.398. The radioactive peroxide was prepared in the same way using commercial acetic-2- $\text{C}^{14}$ -anhydride.

Methyl Iodide: The iodide was washed with thiosulphate solution, dried with calcium chloride and then distilled on a Todd column. The purity was checked by gas-chromatographic analysis. The samples were kept in the dark both before and during analysis. 10 ml of radioactive methyl iodide were purified as above; the specific activity was measured by scintillation counting, and found to be  $16.4 \mu$  curies/ $\mu\text{mole}$ .

**Radioactive Methyl Bromide:** Radioactive methyl bromide was prepared from C-14 methanol by reaction with red phosphorus and bromine. Thus prepared, methyl bromide was passed through a calcium chloride column, then condensed and shaken with red phosphorus. It was finally purified by passing through concentrated sulphuric acid and then over potassium hydroxide pellets. The gas was stored in a blackened glass bulb.

## Results and Discussion

### Methyl Iodide-Methyl Radical Exchange.

**Reactions in Iso-octane Solution.** The first series of experiments was carried out with solutions of non-labelled methyl iodide in iso-octane, using radioactive acetyl peroxide as the source of  $\text{C}^{14}\text{H}_3$  radicals. The experimental results obtained in this system are listed in table 2, and the plots of  $\log(k_2/k_1)$  against  $1/T$  give a straight line corresponding to  $E_2 - E_1 = -3.2$  kcal/mole for iso-octane and  $E_2 - E_1 = -1.8$  kcal/mole for toluene.

Inspection of table 2 shows that the amount of methane formed in the presence of methyl iodide is larger than that produced in its absence, whereas the amounts of  $\text{CO}_2$  or ethane obtained in the process remained unchanged. This observation suggests that a metathetic reaction of solvent radicals ( $\text{C}_8\text{H}_{17}\cdot$ ) with methyl iodide produces additional methyl radicals and consequently additional methane. However, detailed consideration of the data proves that a simple mechanism which includes reaction (4),



in addition to reactions (1) and (2) is not sufficient to account for the observed facts. Reaction (4) in conjunction with reaction (1) regenerates iso-octyl radicals, and thus, if no other changes take place in the system, their stationary concentration should remain unaltered and the rate of methane formation should increase linearly with the concentration of the added methyl iodide. This, however, is not the case.

Table 2. Methyl Iodide; Iso-Octane

carried out with radioactive acetyl peroxide

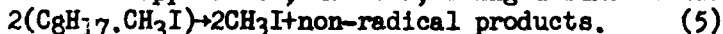
temp. °C	mole % MeI	$\text{CH}_4$	$\text{CO}_2$	$\text{C}^{14}\text{H}_4$ c.p.m.	$k_2/k_1$
54.9	0	225	358	3627	-
54.9	0	228	366	3642	-
54.9	.195	309	344	2753	164
54.9	.387	320	330	2221	163
54.9	.581	346	423	1962	146
					<hr/> 155±6
65.7	0	298	421	4569	-
65.7	0	291	410	4631	-
65.7	0.195	400	424	3659	132
65.7	.387	420	424	2931	146
65.7	.581	458	427	2577	134
65.7	.773	483	418	2308	128
					<hr/> 136±5

Table 2. (Continued)

temp. °C	mole % MeI	CH <sub>4</sub>	CO <sub>2</sub>	C <sup>14</sup> H <sub>8</sub> c.p.m.	k <sub>2</sub> /k <sub>1</sub>
75.8	0	213	-	3306	-
75.8	0	213	355	3311	-
75.8	.291	315	338	2533	105
75.8	.485	328	327	2215	108
75.8	.677	333	330	1862	101
75.8	.773	333	358	1792	114
					<hr/> 107±3
84.8	0	346	500	5326	-
84.8	0	335	485	5504	-
84.8	.387	500	506	3958	92
84.8	.487	504	-	3639	97
84.8	.581	529	496	3632	82
84.8	.773	552	485	3205	87
					<hr/> 90±3
85.0	0	339	511	5497	-
85.0	0	342	491	5418	-
85.0	.387	488	500	3897	103
85.0	.678	529	467	3143	107
85.0	.773	547	487	2967	107
					<hr/> 106±2

The increase in  $\Delta(\text{CH}_4)$  seems to show a saturation behaviour—addition of a small amount of methyl iodide results in a relatively large  $\Delta(\text{CH}_4)$ , but further increase in the  $\text{CH}_3\text{I}$  concentration leads to a relatively small additional increase in  $\Delta(\text{CH}_4)$ . We shall suggest now a tentative explanation of this phenomenon.

The past experiments from this laboratory have shown that iso-octyl radicals decay in solution through a bimolecular disproportionation process. We propose now that in the presence of methyl iodide they may also undergo an association forming a complex iso-C<sub>8</sub>H<sub>17</sub>.CH<sub>3</sub>I, i.e., iso-octyl radical solvated by methyl iodide. We shall assume that such a complex is relatively stable and only slowly decomposes into iso-octyl iodide and a methyl radical, the main mode for its disappearance, however, being a bimolecular reaction (5),



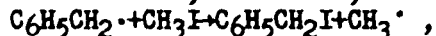
The slowness of the complex decomposition could be attributed to the considerable endothermicity of this process. In this respect the interaction of CH<sub>3</sub> with CH<sub>3</sub>I would be expected to differ. The exchange reaction is thermoneutral and is therefore assumed to be much more rapid than reaction (4); hence the accumulation of CH<sub>3</sub>I·CH<sub>3</sub> complex would not be expected. Now, if most of the iso-octyl radicals are converted into the complex when the mole fraction of methyl iodide is as low as 0.5 mole %, a further increase in CH<sub>3</sub>I concentration should have little effect on the rate of methane formation. This then accounts for the observed levelling behaviour of  $\Delta(\text{CH}_4)$  in the CH<sub>3</sub>I-iso-octane system.



Although the suggested idea is rather unconventional, it is not without some justification. For example, studies of Russell and Simons<sup>11</sup> on I atoms recombination showed that ethyl iodide acts as a very efficient "third body" which might indicate an efficient complex formation between I atoms and ethyl iodide. Formation of relatively stable complexes between free chlorine atoms and various solvents has been recently postulated by Russell and his work substantiated this idea.<sup>12</sup> His mechanism requires the occurrence of a reaction analogous to reaction (5) in order to account for the stationary concentration of chlorine atoms. This is obvious, although not explicitly stated in Russell's papers.

#### Reactions in Toluene Solution

The second series of experiments was carried out in toluene solution. In this solvent no additional amounts of methane were formed in the presence of methyl iodide. One has to conclude, therefore, that the reaction,



is very slow since its endothermicity is too great. It should be stressed that the amounts of carbon dioxide and ethane formed by the decomposition remained remarkably constant on the addition of methyl iodide which shows that the presence of the halide does not affect the peroxide decomposition. All the pertinent data are given in table 3. The constancy of the specific activity of methane formed in the "blanks" is noteworthy and indicative of reliable experimental procedure.

Table 3

Methyl Iodide+Toluene; Carried Out with Radioactive Acetyl Peroxide

T°C	Peroxide conc. $\times 10^2$ M	mole % MeI	CH <sub>4</sub>	CO <sub>2</sub>	C <sup>14</sup> H <sub>4</sub> c.p.m.	k <sub>2</sub> /k <sub>1</sub>
85.4	0.25	0	313	589	5111	-
85.4	0.25	0.673	309	593	4068	37.9
85.4	0.25	1.989	314	601	2856	38.9
85.4	0.25	2.635	315	592	2543	37.3
85.4	0.25	3.273	313	602	2191	39.4
					av. k <sub>2</sub> /k <sub>1</sub> =	38.4 ± 0.8
Specific Activity of C <sup>14</sup> H <sub>4</sub> in Blank = 8.72 $\times 10^8$					c.p.m./mole	
75.6	0.25	0	303	561	5064	-
75.6	0.25	0	292	542	5023	-
75.6	0.25	1.336	303	551	3194	42.8
75.6	0.25	1.989	299	554	2670	43.8
75.6	0.25	2.635	303	553	2402	40.6
75.6	0.25	3.273	305	553	2091	41.7
					av. k <sub>2</sub> /k <sub>1</sub> =	42.2 ± 1.1
Specific Activity of C <sup>14</sup> H <sub>4</sub> in Blank = 9.00 $\times 10^8$					c.p.m./mole	

Table 3. (Continued)

T°C	Peroxide conc. $\times 10^2$ M	mole % MeI	CH <sub>4</sub>	CO <sub>2</sub>	C <sup>14</sup> H <sub>4</sub> c.p.m.	k <sub>2</sub> /k <sub>1</sub>
65.2	1.25	0	335	592	5547	-
65.2	1.25	0	335	595	5574	-
65.2	1.25	1.336	335	591	3484	44.0
65.2	1.25	1.989	337	569	2875	46.0
65.2	1.25	2.635	338	576	2524	44.4
					av. k <sub>2</sub> /k <sub>1</sub> =	44.8 $\pm$ .8
Specific Activity of C <sup>14</sup> H <sub>4</sub> in Blank = 8.90 $\times 10^8$ c.p.m./mole						
65.2	0.26	0	317	594	5342	-
65.2	0.26	0	318	562	5234	-
65.2	0.26	1.989	319	599	2760	45.1
65.2	0.26	2.635	319	603	2363	45.7
					av. k <sub>2</sub> /k <sub>1</sub> =	45.4 $\pm$ .3
Specific Activity of C <sup>14</sup> H <sub>4</sub> in Blank = 8.90 $\times 10^8$ c.p.m./mole						
55.0	1.25	0	292	526	4800	-
55.0	1.25	0	292	524	4878	-
55.0	1.25	0.673	296	536	3690	48.0
55.0	1.25	1.336	292	520	2900	49.4
55.0	1.25	1.989	292	514	2443	48.3
55.0	1.25	2.635	295	513	2105	48.0
55.0	1.25	3.273	296	515	1787	50.5
					av. k <sub>2</sub> /k <sub>1</sub> =	48.8 $\pm$ .3
Specific Activity of C <sup>14</sup> H <sub>4</sub> in Blank = 8.78 $\times 10^8$ c.p.m./mole						

Two series of experiments were carried out at 65°C at concentrations of 0.26 $\times 10^{-2}$  M and 1.25 $\times 10^{-2}$  M of acetyl peroxide. The excellent agreement between the respective k<sub>2</sub>/k<sub>1</sub> values supports strongly the proposed mechanism. On the whole, the degree of reproducibility in each series of experiments was gratifying and consequently this system, i.e., toluene and not iso-octane solution, was chosen for experiments involving other halides. These are reported in the second paper.

To provide a further check of the method, several experiments were carried out with C<sup>14</sup>H<sub>3</sub>I and a non-labelled acetyl peroxide. The results are given in table 4. Although the reproducibility was not as good as that obtained by the previous technique, the data given in the last column of table 4 leave no doubt about the reliability of the proposed mechanism.

Comparison of the k<sub>2</sub>/k<sub>1</sub> values obtained in iso-octane and in toluene solution is instructive. The former should be denoted as k<sub>2</sub>/k<sub>1, iso-octane</sub>, while the latter represent k<sub>2</sub>/k<sub>1, toluene</sub>. Their ratio is therefore k<sub>1, toluene</sub>/k<sub>1, iso-octane</sub> and characterizes the two solvents only. This ratio was obtained in other reactions described elsewhere<sup>5</sup> and its value at, e.g., 85°C was found to be about 3.0. This agrees well with the value of 2.5 derived from the present experiments, showing that the peculiar side reactions observed in iso-octane solution have no effect upon the exchange reaction.

Table 4. System  $C^{14}H_3I + CH_3$  in Toluene Solution

$T = 65.2^\circ C$ ; peroxide conc.  $1.5 \times 10^{-2} M$ ;  
specific activity of  $CH_3I = 3.62 \times 10^4$  c.p.m./mmole

mole % $Me^{14}I$	total $CH_4$ mmole $\times 10^3$	total activity c.p.m.	$k_2/k_1$
5.14	15.7	361	32
5.14	15.8	405	45
6.34	15.8	458	58
6.34	15.8	441	50
		av.	46 $\pm$ 5

Methyl Bromide-Methyl Radical Exchange

The exchange reaction  $CH_3Br + \cdot CH_3 \rightarrow CH_3 + BrCH_3$  was found to be much slower than the analogous reaction of methyl iodide. Consequently, the technique based on  $C^{14}H_3$  radicals was found to be impractical since the "loss" in the methane radioactivity was too low to be measured with any degree of accuracy. Therefore, this reaction was studied only by the alternative technique, i.e., the one using a labelled methyl bromide. Moreover, in view of the slowness of this reaction, a high specific activity of  $C^{14}H_3Br$  was required in order to get a measurable activity of the formed methane. This increased the cost of such an investigation and imposed a severe restriction on the number of experiments which could be carried out. The results were obtained at two temperatures only, namely  $70^\circ C$  and  $80^\circ C$ , and the pertinent data are listed in table 5. The rate of exchange is lower by nearly four powers of ten when compared to that observed in the methyl iodide system. It should be noticed also that  $E_2 - E_1$  is definitely positive for the methyl bromide exchange while the corresponding activation energies difference in the reaction involving methyl iodide is negative and amounts to  $-1.8$  kcal/mole.

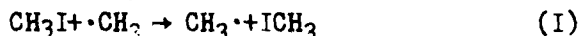
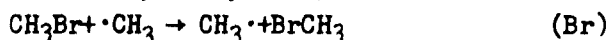
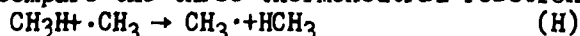
Table 5. System  $C^{14}H_3Br + CH_3$  in Toluene Solution

specific activity of  $Me^{14}Br = 7.15 \times 10^7$  c.p.m./mmole (determined by conversion of  $MeBr$  into  $MeH$ ); toluene = 47.0 mmole

$T^\circ C$	[peroxide] $\times 10^2 M$	$C^{14}H_3Br$ mmole	amount of $CH_4$ mmole $\times 10^3$	activity c.p.m.	$k_2/k_1$ $\times 10^3$
70.0	1.7	0	31.9	-	-
70.0	1.7	0	31.6	-	-
70.0	1.7	1.875	31.6	802 $\pm$ 15	8.9
70.0	1.7	2.26	31.6	946 $\pm$ 15	8.7
80.4	0.39	0	24.7	-	-
80.4	0.39	0.666	24.5	353 $\pm$ 8	14.2
80.4	0.39	0.955	24.5	503 $\pm$ 12	14.2
80.4	0.39	1.441	24.5	646 $\pm$ 14	12.0

### Discussion of the Thermoneutral Exchanges Involving CH<sub>3</sub> Radicals.

It is desirable to compare the three thermoneutral reactions



Reaction (H) was investigated by McNesby and Gordon,<sup>13</sup> and by Dainton, Ivin and Wilkinson.<sup>14</sup> Both groups studied the reaction in the gas phase; the former workers used CD<sub>3</sub> radicals to attack CH<sub>4</sub>, while the latter team worked with C<sup>14</sup>H<sub>4</sub>. Extrapolating the reported results to 65°C, and using Price and Trotman-Dickenson<sup>15</sup> data on the rate of the reaction CH<sub>3</sub>· + C<sub>6</sub>H<sub>5</sub>.CH<sub>3</sub> → CH<sub>4</sub> + C<sub>6</sub>H<sub>5</sub>.CH<sub>2</sub>·, we calculate

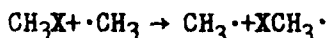
$$k_{\text{H}}/k_1 = 4 \times 3.10^{-3} \quad \text{from the McNesby and Gordon data,}$$

and

$$k_{\text{H}}/k_1 = 4 \times 2.10^{-3} \quad \text{from Dainton et al.'s data.}$$

It would be expected that the rate constant of the thermoneutral exchange reaction should increase with decreasing C-X bond dissociation energy. This is the case, as shown by the data given in table 6. However, the enormous decrease in the bond dissociation energies (about 35 kcal/mole) when Br is substituted for H in methane results only in a small increase in the rate constant (by a factor of 2-3).

Table 6. Comparison of Thermoneutral Exchange Reaction



all the rate constants refer to 65°C

X	$k_2, X/k_1$	D(C-X) kcal/mole	$\Delta E$ kcal/mole	$\Delta D(\text{C-X})$ kcal/mole
H	$2-3 \times 10^{-3}$	101-102		
Br	$6 \times 10^{-3}$	67	0.5	35
I	45	54	5.8	13

On the other hand, substituting I for Br increases the rate constant of the exchange by a factor of 7500, although the dissociation energy of the ruptured bond is decreased by only 13 kcal/mole. If the reasonable assumption is made that the change in the rate constant is caused by the variation in the activation energy, one finds  $\Delta E_{\text{Br}, \text{I}} = E_{2, \text{Br}} - E_{2, \text{I}}$  to be approximately one half  $D(\text{CH}_3\text{-Br}) - D(\text{CH}_3\text{-I})$ . It will be shown in the following paper that this relation seems to hold for other pairs of similar reactions. In contradistinction,  $\Delta E_{\text{H}, \text{Br}} = E_{2, \text{H}} - E_{2, \text{Br}}$  is a negligible fraction of  $D(\text{CH}_3\text{-H}) - D(\text{CH}_3\text{-Br})$ . Therefore, H abstraction by CH<sub>3</sub> radicals proceeds relatively much faster than the analogous abstraction of halogen atoms, and in the following paper it will be shown that the slow abstraction of a halogen atom is due to a repulsion between the CH<sub>3</sub> radical and a "stretched" H<sub>3</sub>C-X molecule. Apparently such a repulsion is very small for X = H.

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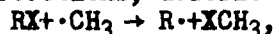
## Abstraction of Halogen Atoms by Methyl Radicals

### Part 2. Reaction $RX + CH_3 \rightarrow R + XCH_3$ for R Different from Methyl

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Halogen abstraction reactions, described by the equation



were investigated in solution for  $R = C_2H_5$ ,  $iso-C_3H_7$ ,  $t-C_4H_9$ ,  $PhCH_2$ ,  $CH_2Cl$ ,  $CHCl_2$ ,  $CCl_3$  and  $CF_3$ . For a few compounds the reaction was investigated over a sufficient range of temperature to permit us to determine the respective activation energies.

It was found that the Br abstraction from  $CCl_3Br$  proceeds about 1000 times faster than that from  $PhCH_2Br$  in spite of the fact that the respective C-Br bond dissociation energies are nearly equal. Similarly, the I abstraction from  $CF_3I$  was found to be about 500 times faster than that from  $CH_3I$ , although  $D(CH_3-I)$  is again nearly equal to  $D(CF_3-I)$ . These observations led to a notion that the repulsion between the approaching  $CH_3$  radical and the stretched C-X bond is an important factor in determining the rate of abstraction. This problem is discussed in more detail, and the effect of electron-withdrawing groups upon the repulsion and the rate of abstraction is considered.

Some data concerned with H abstraction are accumulated and their significance is discussed.

## INTRODUCTION

In part 2 of this series we report the kinetics of the reactions



where R is other than  $CH_3$ . This greatly simplifies the experimentation. The labelling, which was necessary in studies of the exchange reactions described in Part I, is not required as now advantage may be taken of the fact that the halogen-atom abstraction decreases the yield of methane. This results from competition of the investigated reaction (2) with reaction (1),



in which the methyl radical abstracts a hydrogen atom from toluene used as solvent in all these experiments. If the stationary concentration of  $CH_3$  radicals is maintained at a sufficiently low level, all the methyl radicals which escape from the "cage" are consumed either in reaction (1) or (2) and none undergoes recombination with radicals present in the system. Under these conditions the ratio  $k_2/k_1$  is determined by the

$$k_2/k_1 = \{ (CH_4 \text{ lost}) / (CH_4 \text{ formed}) \} / \{ X_{\text{toluene}} / X_{RX} \},$$

where  $(\text{CH}_4 \text{ formed})$  denotes the amount of methane formed in the experiment,  $(\text{CH}_4 \text{ lost})$  is the difference between the amount of methane formed in the "blank", i.e., in an identical experiment carried out in the absence of RX, and that formed in the relevant experiment, and  $X_{\text{toluene}}$  and  $X_{\text{RX}}$  are the mole fractions of toluene and RX respectively. The validity of this scheme was amply demonstrated in numerous publications from this laboratory<sup>1-3</sup> in which "methyl affinities" of aromatic hydrocarbons, olefins, etc., were reported.

In most experiments described in this paper, methyl radicals were generated by thermal decomposition of acetyl peroxide; however, in some cases photolysis of azomethane was used as an alternative source. It is important to stress that the same kinetic constants were derived from photolysis experiments as from those in which  $\text{CH}_3$  radicals were generated by the decomposition of acetyl peroxide.<sup>4,5</sup> The present work furnishes other examples of such an agreement.

In deriving the expression for  $k_2/k_1$  given above, the possibility of  $\text{CH}_3$  radicals reacting with the substrate to produce methane was neglected. This eventuality was considered elsewhere.<sup>6,3</sup> It was shown that in such a case the right side of the expression for  $k_2/k_1$ , now referred to as  $(k_2/k_1)_{\text{expt.}}$ , is no longer constant, but its reciprocal varies linearly with  $X_{\text{RX}}/X_{\text{toluene}}$ , the intercept giving the correct  $k_1/k_2$  value, whilst the slope is given by  $k_3/k_2$ . The results of this study show that such a linear relation is observed when  $\text{CH}_2\text{ClBr}$  or  $\text{CHCl}_2\text{Br}$  are the substrates. On the other hand, in reactions involving ethyl iodide or isopropyl iodide the constancy of  $k_2/k_1$  proves that the abstraction of H atoms from these substrates is negligible when compared with I abstraction.

### Results

The experimental technique is described in ref. (3) and (4), and therefore need not be reported here. The reason for the use of toluene as solvent has been clearly explained in Part I. All the substrates used in this study were carefully purified by conventional methods and their degree of purity ascertained by V.P.C. Any trace of iodine was rigorously removed from the investigated compounds, and the samples were stored in darkness. Solutions of the iodides were handled in dim light and protected from daylight during experiments.

The pertinent results are presented in tables 7, 8 and 9. Most of the experiments were performed in acetyl peroxide systems. In fact, photolysis of azomethane could not be used in studies of iodide reactions as these compounds absorb light in the same region as azomethane does and undergo subsequent decomposition. The photolysis technique was feasible, however, in studies of bromide reactions. For example, using Corning filter no. 52, it was possible to prevent the photolysis of  $\text{CHCl}_2\text{Br}$  without interfering excessively with the photolysis of azomethane.

Table 7.  $\text{RI} + \text{CH}_3\cdot \rightarrow \text{R}\cdot + \text{CH}_3\text{I}$ ; Solvent, Toluene

$T^\circ\text{C}$	peroxide $10^2 \text{ M}$	RI mole % $\text{C}_2\text{H}_5\text{I}$	$\text{CH}_4$ mm Hg	$k_2/k_1$
45.0	1.5	0	2.48	-
45.0	1.5	0	2.48	-
45.0	1.5	0.263	1.54	231
45.0	1.5	0.395	1.32	222
45.0	1.5	0.658	0.976	233
			average	$229 \pm 6$
54.8	3.7	0	1.90	-
54.8	3.7	0	1.90	-
54.8	3.7	0.263	1.25	197
54.8	3.7	0.526	0.941	193
54.8	3.7	0.658	0.810	204
			average	$198 \pm 4$
65.2	0.37	0	3.47	-
65.2	0.37	0	3.50	-
65.2	0.37	0.132	2.82	178
65.2	0.37	0.263	2.365	179
65.2	0.37	0.395	1.99	189
65.2	0.37	0.526	1.81	175
65.2	0.37	0.658	1.60	177
			average	$179 \pm 3$
65.2	3.0	0	1.96	-
65.2	3.0	0	1.96	-
65.2	3.0	0.395	1.14	181
65.2	3.0	0.526	1.00	182
65.2	3.0	0.658	0.884	185
			average	$183 \pm 2$
75.8	0.74	0	1.77	-
75.8	0.74	0	1.77	-
75.8	0.74	0.263	1.23	166
75.8	0.74	0.395	1.06	169
75.8	0.74	0.526	0.94	167
75.8	0.74	0.658	0.85	163
			average	$166 \pm 2$
75.6	1.1	0	1.77	-
75.6	1.1	0.395	1.04	178
75.6	1.1	0.526	0.922	174
75.6	1.1	0.658	0.837	168
			average	$173 \pm 4$



Table 7.  $RI+CH_3\cdot \rightarrow R\cdot+CH_3I$ ; Solvent, Toluene (Continued)

T°C	peroxide $10^2$ M	RI mole % $C_2H_5I$	$CH_4$ mm Hg	$k_2/k_1$
84.9	0.50	0	0.740	-
84.9	0.50	0.395	0.456	157
84.9	0.50	0.526	0.397	163
84.9	0.50	0.526	0.403	158
			average	$159 \pm 2$
84.8	0.90	0	1.795	-
84.8	0.90	0	1.817	-
84.8	0.90	0.132	1.496	157
84.8	0.90	0.263	1.270	160
84.8	0.90	0.395	1.113	157
84.8	0.90	0.526	0.990	156
84.8	0.90	0.658	0.867	164
84.8	0.90	0.658	0.865	164
			average	$160 \pm 2$
<i>iso-C<sub>3</sub>H<sub>7</sub>I</i>				
45.0	1.75	0	1.863	-
45.0	1.75	0	1.891	-
45.0	1.75	0.101	.884	1,110
45.0	1.75	0.304	.437	1,080
45.0	1.75	0.405	.378	974
			average	$1,055 \pm 50$
44.6	1.75	0	1.693	-
44.6	1.75	0	1.698	-
44.6	1.75	0.0507	1.124	1,005
44.6	1.75	0.0507	1.092	1,095
44.6	1.75	0.0761	.976	970
44.6	1.75	0.0761	.962	1,005
44.6	1.75	0.1014	.819	1,060
44.6	1.75	0.1014	.850	985
			average	$1,020 \pm 40$
55.1	1.75	0	2.528	-
55.1	1.75	0	2.592	-
55.1	1.75	0.0338	1.918	987
55.1	1.75	0.1352	1.092	993
55.1	1.75	0.1690	0.982	950
			average	$977 \pm 25$

Table 7.  $\text{RI} + \text{CH}_3\cdot \rightarrow \text{R}\cdot + \text{CH}_3\text{I}$ ; Solvent, Toluene (Continued)

T <sup>o</sup> C	peroxide $10^2$ M	RI mole %	$\text{CH}_4$ mm Hg	$k_2/k_1$
65.2	0.70	0	2.976	-
65.2	0.70	0	2.969	-
65.2	0.70	0.0761	1.804	851
65.2	0.70	0.1014	1.565	886
65.2	0.70	0.2028	1.082	860
65.2	0.70	0.3041	0.828	849
65.2	0.70	0.4055	0.640	895
			average	868 $\pm$ 20
75.8	0.35	0	2.401	-
75.8	0.35	0	2.443	-
75.8	0.35	0.1014	1.438	675
75.8	0.35	0.2028	1.000	700
75.8	0.35	0.4055	0.640	684
			average	686 $\pm$ 10
85.2	0.23	0	2.146	-
85.2	0.23	0	2.161	-
85.2	0.23	0.0675	1.508	643
85.2	0.23	0.135	1.166	626
85.2	0.23	0.135	1.145	651
85.2	0.23	0.338	0.724	583
			average	625 $\pm$ 20
$t\text{-C}_4\text{H}_9\text{I}$				
65.2	0.42	0	1.918	-
65.2	0.42	0	1.703	-
65.2	0.42	0.0516	0.937	1,780
65.2	0.42	0.1032	0.602	1,960
			average	1,870 $\pm$ 100
$\text{Ph}\cdot\text{CH}_2\text{I}$				
65.0	0.51	0	1.782	-
65.0	0.51	0.0162	0.810	7,390
65.0	0.51	0.0325	0.511	7,680
65.0	0.51	0.0486	0.371	7,800
65.0	0.51	0.0486	0.384	7,470
65.0	0.51	0.0650	0.302	7,510
65.0	0.51	0.0812	0.250	7,540
			average	7,580 $\pm$ 100

Table 7.  $\text{RI} + \text{CH}_3 \cdot \rightarrow \text{R} \cdot + \text{CH}_3\text{I}$ ; Solvent, Toluene (Continued)

T°C	peroxide $10^2$ M	RI mole %	$\text{CH}_4$ mm Hg	$k_2/k_1$
65.0	0.51	0	2.713	-
65.0	0.51	0	2.750	-
65.0	0.51	0.0162	1.208	7,760
65.0	0.51	0.0162	1.234	7,470
65.0	0.51	0.0325	0.787	7,600
65.0	0.51	0.0486	0.573	7,730
65.0	0.51	0.0486	0.564	7,880
65.0	0.51	0.0650	0.458	7,640
			average	7,680 $\pm$ 100

 $\text{CH}_2\text{ClI}$ 

65.2	0.42	0	3.648	-
65.2	0.42	0.0114	2.179	5,900
65.2	0.42	0.0128	1.613	5,500
65.2	0.42	0.0343	1.071	7,000
65.2	0.42	0.0571	0.728	7,000
			average	6,400 $\pm$ 500

 $\text{CF}_3\text{I}$ 

65.2	0.15	0	2.137	-
65.2	0.15	0	2.200	-
65.2	0.15	0.00378	1.166	22,600*
65.2	0.15	0.00890	0.774	21,800*
65.2	0.15	0.0099	0.760	20,200*
65.2	0.15	0.0176	0.504	21,500*
			average	21,500 $\pm$ 800

\* Not corrected for  $\text{CF}_3\text{I}$  consumed. Corrections are less than 25% for the lowest concentration of  $\text{CF}_3\text{I}$  and progressively smaller for higher concentrations.

Table 8.  $\text{RBr} + \text{CH}_3 \cdot \rightarrow \text{R} \cdot + \text{CH}_3\text{Br}$ ; Solvent, Toluene  
 $\text{CH}_2\text{ClBr}$ 

T°C	peroxide $10^2$ M	RBr mole %	$\text{CH}_4$ mm Hg	$k_2/k_1$ **
48.5	3.6	0	3.287	-
48.5	3.6	0	3.291	-
48.5	3.6	7.5	3.070	0.87
48.5	3.6	15.4	2.921	0.69
48.5	3.6	41.1	2.434	0.50
48.5	3.6	52.2	2.304	0.39
		extrapolated to zero conc.		0.90

Table 8.  $RBr + CH_3 \rightarrow R + CH_3Br$ ; Solvent, Toluene (Continued)

T°C	peroxide $10^2 M$	$CH_2ClBr$		
		RBr mole %	$CH_4$ mm Hg	$k_2/k_1^{**}$
77.1	0.29	0	1.06	-
77.1	0.29	0	1.06	-
77.1	0.29	7.55	0.941	1.46
77.1	0.29	15.4	0.874	1.17
77.1	0.29	29.0	0.801	0.788
77.1	0.29	41.1	0.740	0.615
77.1	0.29	52.2	0.706	0.459
extrapolated to zero conc.				1.75
$CHCl_2Br$				
65.2	0.75	0	2.30	-
65.2	0.75	0	2.30	-
65.2	0.75	0.520	1.46	109
65.2	0.75	1.55	0.941	91.2
65.2	0.75	3.52	0.658	68.3
65.2	0.75	4.68	0.591	58.8
65.2	0.75	5.58	0.545	51.9
extrapolated to zero conc.				124
77.1	0.29	0	1.06	-
77.1	0.29	0	1.06	-
77.1	0.29	0.520	0.689	103
77.1	0.29	1.04	0.533	94
77.1	0.29	1.55	0.438	89.7
77.1	0.29	2.60	0.345	78.0
77.1	0.29	3.10	0.324	70.9
extrapolated to zero conc.				113
azomethane				
0.0	$2 \cdot 10^{-3} M$	0	1.09*	-
0.0	$2 \cdot 10^{-3} M$	0	1.02*	-
0.0	$2 \cdot 10^{-3} M$	0.520	0.407*	302
0.0	$2 \cdot 10^{-3} M$	1.04	0.350*	191
0.0	$2 \cdot 10^{-3} M$	1.55	0.276*	177
0.0	$2 \cdot 10^{-3} M$	2.07	0.267*	139
0.0	$2 \cdot 10^{-3} M$	3.10	0.215*	121
0.0	$2 \cdot 10^{-3} M$	0	0.396*	-
0.0	$2 \cdot 10^{-3} M$	0.520	0.188*	212
0.0	$2 \cdot 10^{-3} M$	1.04	0.122*	218
0.0	$2 \cdot 10^{-3} M$	1.29	0.111*	195
0.0	$2 \cdot 10^{-3} M$	1.55	0.105*	175
0.0	$2 \cdot 10^{-3} M$	3.10	0.086*	113
both series at 0°C extrapolated to zero conc				328

Table 8.  $\text{RBr} + \text{CH}_3 \rightarrow \text{R} + \text{CH}_3\text{Br}$ ; Solvent, Toluene (Continued)

Temp	peroxide $10^{-2}\text{M}$	RBr mole %	$\text{CH}_4$ mm Hg	$k_2/k_1^{**}$
azomethane				
25.5	$2.10 \cdot 10^{-3}\text{M}$	0	0.438*	-
25.5	$2.10 \cdot 10^{-3}\text{M}$	0	0.437*	-
25.5	$2.10 \cdot 10^{-3}\text{M}$	0.520	0.221*	187
25.5	$2.10 \cdot 10^{-3}\text{M}$	0.520	0.213*	202
25.5	$2.10 \cdot 10^{-3}\text{M}$	1.04	0.1545*	174
25.5	$2.10 \cdot 10^{-3}\text{M}$	1.55	0.1274*	154
25.5	$2.10 \cdot 10^{-3}\text{M}$	2.98	0.0944*	118
extrapolated to zero conc. 227				
azomethane				
44.6	$2.10 \cdot 10^{-3}\text{M}$	0	0.431*	-
44.6	$2.10 \cdot 10^{-3}\text{M}$	0	0.458*	-
44.6	$2.10 \cdot 10^{-3}\text{M}$	0.520	0.262*	134
44.6	$2.10 \cdot 10^{-3}\text{M}$	1.04	0.199*	118
44.6	$2.10 \cdot 10^{-3}\text{M}$	1.55	0.166*	107
44.6	$2.10 \cdot 10^{-3}\text{M}$	3.10	0.129*	77.2
44.6	$2.10 \cdot 10^{-3}\text{M}$	4.12	0.112*	69.8
extrapolated to zero conc. 154				
azomethane				
65.0	$2.10 \cdot 10^{-3}\text{M}$	0	0.509*	-
65.0	$2.10 \cdot 10^{-3}\text{M}$	0	0.511*	-
65.0	$2.10 \cdot 10^{-3}\text{M}$	0.520	0.309*	124
65.0	$2.10 \cdot 10^{-3}\text{M}$	1.04	0.244*	104
65.0	$2.10 \cdot 10^{-3}\text{M}$	1.55	0.207*	92.7
65.0	$2.10 \cdot 10^{-3}\text{M}$	2.70	0.170*	75.4
65.0	$2.10 \cdot 10^{-3}\text{M}$	3.10	0.153*	72.9
extrapolated to zero conc. 138				
azomethane				
64.6	$2.10 \cdot 10^{-3}\text{M}$	0	0.491*	-
64.6	$2.10 \cdot 10^{-3}\text{M}$	0	0.468*	-
64.6	$2.10 \cdot 10^{-3}\text{M}$	0.520	0.300*	115
64.6	$2.10 \cdot 10^{-3}\text{M}$	1.555	0.200*	88.6
64.6	$2.10 \cdot 10^{-3}\text{M}$	2.50	0.156*	78.2
64.6	$2.10 \cdot 10^{-3}\text{M}$	3.10	0.151*	68.1
64.6	$2.10 \cdot 10^{-3}\text{M}$	4.12	0.134*	60.0
extrapolated to zero conc. 130				
azomethane				
94.5	$2.10 \cdot 10^{-3}\text{M}$	0	0.607*	-
94.5	$2.10 \cdot 10^{-3}\text{M}$	0	0.581*	-
94.5	$2.10 \cdot 10^{-3}\text{M}$	1.04	0.328*	77.4
94.5	$2.10 \cdot 10^{-3}\text{M}$	1.55	0.289*	66.5
94.5	$2.10 \cdot 10^{-3}\text{M}$	2.07	0.255*	62.7
94.5	$2.10 \cdot 10^{-3}\text{M}$	4.46	0.195*	43.8
extrapolated to zero conc. 96				

Table 8.  $\text{RBr} + \text{CH}_3 \rightarrow \text{R} + \text{CH}_3\text{Br}$ ; Solvent, Toluene (Continued)

$T^\circ\text{C}$	peroxide $10^2\text{M}$	RBr mole % $\text{CCl}_3\text{Br}$	$\text{CH}_4$ mm Hg	$k_2/k_1^{**}$
48.5	1.1	0	2.79	-
48.5	1.1	0	2.84	-
48.5	1.1	0.0157	1.37	6710
48.5	1.1	0.0157	1.32	7190
48.5	1.1	0.0314	0.846	7390
48.5	1.1	0.0472	0.616	7560
48.5	1.1	0.0629	0.449	8370
			average	7400
77.2	0.44	0	1.109	-
77.2	0.44	0	1.272	-
77.2	0.44	0.0157	0.548	7450
77.2	0.44	0.0157	0.548	7450
77.2	0.44	0.0472	0.292	6510
			average	$7100 \pm 400$
$\text{Ph}\cdot\text{CH}_2\text{Br}$				
65.0	2.0	0	0.225	-
65.0	2.0	1.88	0.187	7.7
65.0	2.0	2.32	0.201(?)	5.0(?)
65.0	2.0	16.5	0.090	7.6
65.0	1.5	0	0.380	-
65.0	1.5	0	0.372	-
65.0	1.5	8.20	0.219	8.6
65.0	1.5	15.2	0.171	6.7
65.0	1.5	20.3	0.146	6.2
			average	$7.3 \pm 1.0$

\* These numbers denote  $[\text{CH}_4]/[\text{N}_2]$ .

\*\* Whenever H-abstraction and Br-abstraction proceed simultaneously, the values given in this column represent  $(k_2/k_1)_{\text{expt}}$ . These extrapolate to  $k_2/k_1$  for zero concentration.

Table 9.  $\text{CCl}_4 + \text{CH}_3\cdot \rightarrow \text{CCl}_3\cdot + \text{ClCH}_3$ ;  $T = 65^\circ\text{C}$ .

solvent, toluene; conc. of acetyl peroxide  $5 \times 10^{-3}$  M

mole % $\text{CCl}_4$	$\text{CH}_4$ mm Hg	$k_2/k_1$
0	3.13	-
0	3.17	-
10.9	2.05	4.3
10.9	2.10	4.1
21.6	1.45	4.2
21.6	1.44	4.3
32.1	1.04	4.3
	average	$4.2 \pm 0.1$
per Cl atom $k'/k_1 =$		$1.06 \pm 0.03$

Only a few compounds were studied over a sufficient temperature range to permit the determination of the respective activation energies. The data thus obtained serve to show that the  $A_2/A_1$  factors do not differ greatly from each other. Hence, one may attribute the large differences observed in the relevant  $k_2/k_1$  values to energy factors rather than to entropy factors.\* All the available data for  $E_2 - E_1$  and  $A_2/A_1$  are listed in table 10.

Table 10. Activation Energies  $E_2 - E_1$  and Frequency Factors  $A_2/A_1$

subscript 1 refers to the reaction  $\text{C}_6\text{H}_5\cdot\text{CH}_3 \rightarrow \text{CH}_4 + \text{C}_6\text{H}_5\cdot\text{CH}_2$

reaction	$E_2 - E_1$ kcal/mole	$A_2/A_1$
$\text{CH}_3\text{I} + \text{CH}_3\cdot \rightarrow \text{CH}_4 + \text{ICH}_3$	$-1.8 \pm 0.5$	3.0
$\text{C}_2\text{H}_5\text{I} + \text{CH}_3\cdot \rightarrow \text{C}_2\text{H}_6 + \text{ICH}_3$	$-1.8 \pm 0.5$	14.7
$\text{iso-C}_3\text{H}_7\text{I} + \text{CH}_3\cdot \rightarrow \text{iso-C}_3\text{H}_8 + \text{ICH}_3$	$-3.4 \pm 1.0$	5.4
$\text{CHCl}_2\text{Br} + \text{CH}_3\cdot \rightarrow \text{CHCl}_2 + \text{ICH}_3$	$-2.6 \pm 0.5$	2.9

Hydrogen-atom abstraction from the substrate was noticed in reactions involving  $\text{CH}_2\text{ClBr}$  and  $\text{CHCl}_2\text{Br}$ . The plots of  $(k_2/k_1)_{\text{expt.}}^{-1}$  against  $X_{\text{RBr}}/X_{\text{toluene}}$  give a straight line, and the data for  $k_3/k_2$  and  $k_3/k_1$  are given in table 11. Undoubtedly, hydrogen abstraction takes place in the benzyl-bromide reaction. However, the experimental scatter of these data obscure the trend in the corresponding values of  $(k_2/k_1)_{\text{expt.}}$

\* Although the experimental values  $E_2 - E_1$  for  $\text{CH}_3\text{I}$  and  $\text{C}_2\text{H}_5\text{I}$  were identical, we are inclined to believe that this results from experimental uncertainties (each of these values is uncertain within  $\pm 0.5$  kcal/mole).

Table 11. Relative Rate Constant of Hydrogen Abstraction Reaction  $k_3$ 

RBr	T°C	$k_3/k_2$	$k_3/k_1$	$(k_3/k_1)$ per act. H
CH <sub>2</sub> ClBr*	48.5	1.3	1.2	0.6
CH <sub>2</sub> ClBr*	77.1	1.5	2.6	1.3
CHCl <sub>2</sub> Br**	0.0	0.175(?)	57(?)	57(?)
CHCl <sub>2</sub> Br**	25.5	0.13	30	30
CHCl <sub>2</sub> Br**	44.6	0.19	29	29
CHCl <sub>2</sub> Br**	65.0	0.21	30	30
CHCl <sub>2</sub> Br**	64.6	0.21	27	27
CHCl <sub>2</sub> Br*	65.2	0.18	23	23
CHCl <sub>2</sub> Br*	77.1	0.16	18	18
CHCl <sub>2</sub> Br**	94.5	0.26	25	25

\* CH<sub>3</sub> produced by thermal decomposition of acetyl-peroxide.

\*\* CH<sub>3</sub> produced by photolysis of azomethane.

The trend in  $k_2/k_1$  values observed in the series CH<sub>3</sub>I, C<sub>2</sub>H<sub>5</sub>I, iso-C<sub>3</sub>H<sub>7</sub>I, and t-C<sub>4</sub>H<sub>9</sub>I was anticipated, and could be predicted from the general behaviour of these halides. In fact, we investigated this series in order to test the experimental method and to substantiate other results reported in this paper. The decrease in the R-I bond dissociation energy, as R varies from CH<sub>3</sub> to C<sub>2</sub>H<sub>5</sub>, iso-C<sub>3</sub>H<sub>7</sub>, and t-C<sub>4</sub>H<sub>9</sub>, is the main cause of the increase in the respective rates of I abstraction. This factor affects the activation energy of the process, and the data listed in table 4 seem to confirm this conclusion although their experimental uncertainties are larger than is desirable.

Studies of halogenated methyl iodides and bromides shed light on some interesting problems. The increase in the rate of Br abstraction with increasing halogenation of the molecule again reflects the effect of decreasing C-Br bond dissociation energy. However, the change in bond dissociation energy is not the only factor which influences the rates. For example, although the values for D(Ph.CH<sub>2</sub>-Br) and D(CCl<sub>3</sub>-Br) are similar, the former having been determined as 50-51 kcal/mole and the latter as 49 kcal/mole,<sup>7</sup> the corresponding  $k_2/k_1$  at 65°C differ enormously, namely,  $k_2/k_1 = 7$  for benzyl bromide and 7400 for trichlorobromomethane. A comparison of the reactivities of methyl iodide and trifluoromethyl iodide is even more striking. Probably, D(CH<sub>3</sub>-I)  $\approx$  D(CF<sub>3</sub>-I), or if we rely on the recent compilation by Errede,<sup>8</sup> the CF<sub>3</sub>-I bond dissociation energy may be even slightly larger than that of the CH<sub>3</sub>-I bond. In spite of this, at 65°C the rate of I abstraction from CF<sub>3</sub>I is about 500 times faster than from CH<sub>3</sub>I. The surprisingly large rate constant of I abstraction from CF<sub>3</sub>I explains the success of Haszeldine's synthesis technique based on addition of this compound to a variety of olefins and olefin derivatives.

Before proceeding further with this discussion, let us consider the data presented in table 12. It is known that differences between D(R-Br) and D(R-I) are only slightly affected by the nature of R, these being approximately 11-13 kcal/mole. Similar values are found for



Table 12. Relative Rate Constants at 65°C for Reactions

Expressed as Ratio  $k_2/k_1$  where  $k_1$  Refers to the Reaction

R/X	I	Br	Cl	H*
CH <sub>3</sub>	45	$\sim 6 \times 10^{-3}$	-	$4 \times 10^{-3}$ **
C <sub>2</sub> H <sub>5</sub>	180	-	-	$6 \times 10^{-11}$
s-C <sub>3</sub> H <sub>7</sub>	870	-	-	$2 \times 10^{-6}$
t-C <sub>4</sub> H <sub>9</sub>	1680	-	-	18.5
Ph.CH <sub>2</sub>	7560	6.5	-	$3 \times 10^{-33}$ ***
CH <sub>2</sub> Cl	6400	1.4	-	-
CHCl <sub>2</sub>	-	131.	-	-
CCl <sub>3</sub>	-	7400	$4 \times 10^{-1}$	-
CF <sub>3</sub>	$\sim 20,000$	-	-	$4 \times 10^{-2}$ ****

\*Extrapolated from results reported by Steacie, Atomic and Free Radical Reactions (Reinhold, 1954, p. 500). The  $k_1$  was extrapolated from the data of Price and Trotman-Dickenson, J. Chem. Soc. 1958, 4205. However, if the older data for  $k_1$  are taken (see Steacie) all the quoted values decrease by a factor of 10.

\*\*From Dainton, Ivin and Wilkinson, Trans. Faraday Soc., 1959, 55, 929.

\*\*\*This value does not involve any extrapolation.

\*\*\*\*From Pritchard et al., Trans. Faraday Soc., 1956, 52, 849.

$D(R-Cl) - D(R-Br)$ . Now, it appears from the data shown in table 10 that  $k_{2,RI}/k_{2,RBr}$  is about  $10^3$ - $10^4$ , and a similar value is found for  $k_{2,RCI}/k_{2,RBr}$ . Assuming that this ratio is essentially determined by the difference in the respective activation energies, it can be concluded that

$$E_{2,Br} - E_{2,RI} \approx E_{2,RCI} - E_{2,RBr} \approx 5-7 \text{ kcal/mole,}$$

and this is approximately one-half of the difference in the relevant bond dissociation energies. On the other hand, although  $D(R-H) - D(R-Br)$  is about 30-35 kcal/mole, the values for  $k_{2,RH}$  are only slightly smaller than the corresponding values of  $k_{2,Br}$ . Therefore, the abstraction of H atoms proceeds relatively faster than the halogen abstraction, if the large values of the respective C-H bond dissociation energies are taken into account. Apparently, some factor exists which hinders halogen abstraction but which interferes only slightly with H atom abstraction.

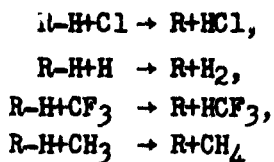
The nature of this factor may be elucidated by the following treatment. The activation energy of the abstraction process can be represented as a sum of two terms: (i) the energy required to stretch the C-X bond to its length in the transition state, and (ii) the repulsion energy required to bring a methyl radical to the stretched C-X bond. The first term decreases along the series R-H, R-Cl, R-Br, and R-I as expected on the basis of decreasing  $D(R-X)$ . The second term contains a contribution

arising from Coulombic repulsion between the p electron of the radical and the closed shell of the halogen atom. The contribution of the repulsion energy is probably negligible in the reaction  $R\cdot + CH_3$  as the shielding of H atom by the electron is slight. Hence, this treatment explains the relatively ready abstraction of hydrogen atoms and the large inertia observed in halogen abstraction.

If the Coulombic repulsion hinders the halogen abstraction, then electron withdrawing groups should lower this barrier and facilitate the abstraction. This indeed seems to be the case. The two examples mentioned earlier may be now discussed in these terms. The electron-withdrawing power of the chlorine substituents makes  $CCl_3Br$  more reactive than  $PhCH_2Br$ . With the more powerful F atoms the effect is even larger as shown by a comparison of the reactivities of  $CH_3I$  and  $CF_3I$ . How potent the  $CF_3$  group is in electron-withdrawing is clearly demonstrated by the exceptional behaviour of  $CF_3I$  in hydrolysis. While  $ROH$  and  $X^-$  are the usual products of  $RX$  hydrolysis,  $CF_3H$  and hypiodite are formed when  $CF_3I$  is the substrate.<sup>9</sup>

It is claimed that the changes in reactivity observed in some radical transfer reactions result from the variable contribution of ionic form to the structure of the respective transition state. For example, the changes in the rates of halogenation are frequently accounted for in these terms—increasing contribution of ionic structure to the transition state seems to facilitate the reaction. One may argue, therefore, that the high reactivity of  $CF_3I$  as compared with  $CH_3I$  results from a greater contribution of the ionic form,  $CF_3^- - I^+ \dots CH_3^+$ , to the transition state of the exchange reaction of  $CF_3I$  than that of a similar structure in the  $CH_3I$  reactions. We doubt whether such an explanation is satisfactory. Ionic forms should be important in sodium-flame reactions where a sodium atom acquires eventually a positive charge. However, the available data show rather small changes in the rates when  $CF_3$  is substituted for  $CH_3$ . Thus, the total number of collisions per effective collision is  $5 \times 10^7$  for  $CH_3F + Na$ ,  $5 \times 10^5$  for  $CH_2F_2 + Na$ ,  $5 \times 10^5$  for  $CHF_3 + Na$ , and still  $5 \times 10^5$  for  $CF_4 + Na$ .<sup>10</sup> The rates of sodium reactions are slightly higher for  $CF_3Br$  or  $CF_3Cl$ <sup>11</sup> when compared with those of  $CH_3Br$  and  $CH_3Cl$ . Of course, there is no point to compare the rates of sodium-flame reactions for  $CF_3I$  and  $CH_3I$ , since both halides essentially react on every collision.<sup>10,11</sup> However, these increases in the rates of sodium-flame reaction were explained by Warhurst<sup>10</sup> in terms of "proximity" effects (acting in addition to any effect which may arise from a change in the respective bond dissociation energy). He assumed that the approaching sodium atom interacts simultaneously with more than one halogen and this interaction decreases the potential-energy barrier. It is our belief that such an effect does not operate in the reactions of methyl radicals, and we intend to check this point in the course of future studies.

Pritchard, Pritchard, Schiff and Trotman-Dickenson<sup>12</sup> pointed out that the following reactions



and

are approximately thermo-neutral. Nevertheless, a chlorine atom is more reactive than a hydrogen atom and the  $CF_3$  radical more reactive than the  $CH_3$  radical. They noticed a correlation between the reactivity and the electro-negativity of the attacking atom or radical and suggested that the increase in the rate is due to decrease in the repulsion experienced by the approaching species. Hence, their ideas are somewhat similar to those discussed in this paper, although there is also an important difference. The decrease in repulsion in our case is due to the polarization of the halogen atom, while in their case it arises from the contribution of ionic form  $R^+ - H \dots ^-Y$ , and this in turn lowers the energy of the repulsion curve.

#### Hydrogen Abstraction Reaction.

In the course of these investigations some information has been obtained about hydrogen-atom abstraction from halogenated methanes. The relevant data are given in table 11. Their accuracy is fair and they permit us to draw some semi-quantitative conclusions about the factors affecting the rate of this process. The presence of a halogen definitely activates the C-H bond and facilitates the H abstraction by  $CH_3$  radicals. The hydrogen abstraction from  $CH_3Cl$ ,  $CH_2Cl_2$ , and  $CHCl_3$  has been investigated,<sup>13</sup> and the results obtained in those studies compare favourably with our findings. At about 60°C the abstraction of an H atom by a  $CH_3$  radical from  $CH_2ClBr$  seems to proceed 3000 times faster than from methane. The abstraction from  $CHCl_2Br$  is faster by a factor of about 30 than the abstraction from  $CH_2ClBr$ . One might conclude, therefore, that at 60°C substitution of each hydrogen atom of methane by a halogen leads to about 30-50 fold increase in the rate of H abstraction by  $CH_3$  radicals.

The studies of Kharasch and of his school showed that  $CH_3$  radicals reacting with chloroform abstract H atoms in preference to Cl atoms. From our data, we can estimate that for this compound at 60°C the rate of H abstraction should be 200 times faster than Cl abstraction. Since the D abstraction proceeds about 12 times slower than H abstraction, the Cl abstraction should be observed in reactions of  $CH_3$  with deuterated chloroform. This indeed was demonstrated in Walling's laboratory.<sup>14</sup> Finally, the calculations show that Br abstraction from bromoform should be comparable to that of hydrogen abstraction. Indeed this conclusion is borne out by Kharasch's qualitative observations. All these data are summarized in table 13 which is self-explanatory. The calculations involve extrapolation and give only the correct order of magnitude. Nevertheless, the emerging pattern of reactivities is clear and interesting.

Table 13. Relative Rates of H Abstraction and X Abstraction  
all the data refer to 65°C

compound	$k_H/k_I$	$k_H/k_{Br}$	$k_H/k_{Cl}$
CH <sub>3</sub> I	$\sim 10^{-3}$	-	-
CH <sub>2</sub> ClI	$\sim 2 \times 10^{-3}$	-	-
CHCl <sub>2</sub> I	$5 \times 10^{-3}$	-	-
CH <sub>3</sub> Br	..	$\sim 10$	-
CH <sub>2</sub> ClBr	..	$\sim 1$	$10^{-3}-10^{-4}$
CHCl <sub>2</sub> Br	..	0.2-0.3	$\sim 10^{-4}$
CH <sub>3</sub> Br	..	$\sim 10$	-
CH <sub>2</sub> Br <sub>2</sub>	..	$\sim 2$	-
CHBr <sub>3</sub>	-	0.6	-
CH <sub>3</sub> Cl	-	-	$\sim 10^4$
CH <sub>2</sub> Cl <sub>2</sub>	-	-	$\sim 10^3$
CHCl <sub>3</sub>	-	-	$\sim 200$

All the values which were not directly determined by experiment were extrapolated on the assumption that the substitution of each H of methane by a halogen increases the reactivity of the remaining hydrogens by approximately a factor of 50.

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### Part 3. The Secondary Deuterium Effect in $\text{CH}_3$ and $\text{CF}_3$ Addition Reactions.

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The secondary deuterium effect was investigated for the  $\text{CH}_3$  and  $\text{CF}_3$  addition reactions. The following results were obtained for the revelant  $k_D/k_H$ .

$\text{CD}_2:\text{CD}_2$	1.05 for $\text{CH}_3$ ,	1.07 for $\text{CF}_3$
$\text{CH}_3.\text{CH}:\text{CD}_2$	1.12 for $\text{CH}_3$ ,	1.07 for $\text{CF}_3$
$\text{CD}_3.\text{CD}:\text{CD}_2$	1.17 for $\text{CH}_3$ ,	1.09 for $\text{CF}_3$
$\text{Ph}.\text{CD}:\text{CD}_2$	1.11 for $\text{CH}_3$ ,	1.10 for $\text{CF}_3$
$\text{CD}_2:\text{CD}.\text{CD}:\text{CD}_2$	1.20 for $\text{CH}_3$ ,	1.09 for $\text{CF}_3$

It is concluded that the incipient  $\text{CH}_3$  (or  $\text{CF}_3$ ) -C bonds in the respective transition states are relatively long, and that the remaining groups around the reactive center retain their original planar configuration. This conclusion does not appear to be invalidated by the recent argument of Wolfsberg.

#### INTRODUCTION

The addition of a radical R to an olefinic or aromatic molecule A yields an adduct radical, as shown by the equation



The relative rate constant of the addition process,  $k_2$ , may be related to the atom localization energy of the most reactive center of the substrate. For example, in the addition of  $\text{CH}_3$  radicals to aromatic non-substituted hydrocarbons, a linear relation was observed for  $\log(k_2/n)$ ,—n being the number of reactive centers—and the respective atom localization energy.<sup>1</sup> Such a relation was previously reported for the addition of  $\text{CCl}_3$  radicals to aromatic hydrocarbons<sup>2</sup> and more recently for the  $\text{CF}_3$  radical addition to the same series of substrates.<sup>3</sup> A linear relation between the rate constant and localization energy was also observed for the addition of  $\text{CH}_3$  radicals to ethylene, styrene, butadiene, vinyl naphthalene, etc.<sup>4,5</sup> The existence of such relations was interpreted as an indication of the formation of an incipient, covalent R-C bond in the transition state of the addition.

The formation of an incipient bond between the radical R and the reactive carbon center of the substrate eventually leads to a rearrangement around this center; i.e., its original planar trigonal configuration is transformed into a tetrahedral one. The question arises, however, to what extent does such a change take place in the transition state. If the

incipient R-C bond is relatively long, the configuration of the other groups around the reaction center should remain planar, but if its length approaches that characterizing the C-R of the final state, then the configuration in the transition state will be tetrahedral.

In order to get some information pertinent to this problem, we decided to investigate the secondary deuterium effect in the radical addition reaction. It was pointed out by Streitwieser<sup>6,7</sup> that the relatively soft out of plane C-H vibration of a trigonal carbon is transformed into a harder bending vibration in a tetrahedral carbon. For such a change, one

calculates the ratio  $k_D/k_H$  for a reaction involving a  $\begin{array}{c} \text{H} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{H} \end{array}$  center to be

1.82 at 65°C. One may expect, therefore, that a value of  $k_D/k_H$  close to unity would indicate a planar transition state and a long R-C bond, whereas if  $k_D/k_H$  is close to 1.82, the configuration around the reactive center in the transition state should be essentially tetrahedral.

The first attempt to utilize this technique for the study of the transition state of radical addition reactions was reported by Matsuoka and Szwarc.<sup>8</sup> They determined the  $k_D/k_H$  ratio for the addition of  $\text{CH}_3$  radicals to  $\alpha,\beta,\beta$ -trideutero styrene and styrene and found its value to be 1.07-1.11. They concluded therefore that the incipient  $\text{CH}_3\text{-C}$  bond is long and the  $\beta$  carbon of styrene retains essentially a planar configuration in the transition state. In the present investigation we extended the work of Matsuoka and Szwarc to other substrates and to additions involving  $\text{CF}_3$  radicals as well as  $\text{CH}_3$  radicals.

#### Experimental.

The following deuterated compounds were investigated:

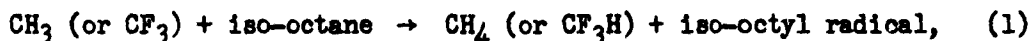
1.  $\text{C}_2\text{D}_4$  acquired from Merck, Montreal; mass-spectrographic analysis showed the presence of  $\sim 3\%$   $\text{C}_2\text{D}_3\text{H}$  and less than 0.1% of  $\text{C}_2\text{H}_4$ . Gas-chromatography showed the absence of chemical impurities.
2.  $\text{CH}_3\text{CH:CD}_2$  acquired from Merck, Montreal. The supplier guaranteed the isotopic purity to be more than 98%. Mass-spectrographic analysis was inconclusive in determining the per cent of  $\text{CH}_3\text{CH:CDH}$  or  $\text{CH}_3\text{CH:CH}_2$ . No chemical impurities were found.
3.  $\text{CD}_3\text{CD:CD}_2$  acquired from Merck, Montreal. Mass-spectrographic analysis showed  $\sim 4\%$  of  $\text{C}_3\text{D}_5\text{H}$  and less than 0.1%  $\text{C}_3\text{H}_8$ . Chemical impurities were absent.
4.  $\text{CD}_2\text{CD:CD:CD}_2$  acquired from Merck, Montreal. Mass-spectrographic analysis showed less than 5% of  $\text{C}_4\text{D}_5\text{H}$ . No chemical impurities were detected.
5.  $\text{Ph.CD:CD}_2$  kindly offered by Dr. Leo Wall of the National Bureau of Standards. The compound was pure chemically and isotopically.

All the gaseous compounds were frozen and thoroughly deaerated before being used for experiments. The hydrogenated compounds were similarly treated. They were all acquired commercially and found to be pure.

Spectroscopic pure-grade iso-octane was used as a solvent. This material was passed through a silica column to remove olefinic impurities and moisture.

Azomethane and hexafluoro azomethane were used for generating radicals. The preparation and handling of these compounds are described

elsewhere.<sup>9,10</sup> In these last two references are also reported all the details of photolysis, the analysis of products, and the calculation of rate constants. The results are given as the ratio  $k_2/k_1$  where the subscripts refer to the reactions (1) and (2) respectively.



The ratio of the heights of the respective mass-spectrographic peaks, determining the masses 16 ( $\text{CH}_4^+$ ) and 28 ( $\text{N}_2^+$ ), was used in determining the relative values of  $\text{CH}_4/\text{N}_2$  used in calculating the relevant  $k_2/k_1$  values for the  $\text{CH}_3$  addition. Similarly, the ratio of the standard gas-chromatogram peaks was used in determining the relative values of  $\text{CF}_3\text{H}/\text{N}_2$ , from which the  $k_2/k_1$  ( $\text{CF}_3$ ) was calculated. The reliability of these techniques was carefully established (see e.g. refs. 10 and 9).

To assure the best precision of the data, solutions of the hydrogenated and deuterated compounds were simultaneously photolyzed and then analyzed. The photolysis of two or three "blanks" (solutions not containing the substrate) was performed at the same time. In studying the addition of methyl radicals identical concentrations of the hydrogenated and deuterated compounds were used, whereas the concentrations of the substrates were varied in studies of  $\text{CF}_3$  radical addition. Both methods seem to be satisfactory for determining  $k_D/k_H$ .

#### Results and Discussion.

All the experimental results are listed in table 14. The last column of this table gives the values of the ratio of the rate constant of the radical addition ( $k_2$ ) to the rate constant of H abstraction ( $k_1$ ). The latter, ( $k_1$ ), is of course constant for the whole series of addition of a particular radical. No attempt was made to determine the temperature coefficient of  $k_2/k_1$ , and all the data were obtained at 65°C.

It is desirable to notice that the investigated compounds differed greatly in their reactivity. The  $k_2$  values for the  $\text{CH}_3$  addition vary by a factor of about 80, and those for the  $\text{CF}_3$  addition show a 12-fold variation in their magnitude. As shown in Table 15, the variation in the reactivity of the individual substrates is not reflected in the  $k_D/k_H$  ratio. The latter were calculated as  $\{(k_2/k_1) \text{ for a deuterated substrate} / (k_2/k_1) \text{ for the hydrogenated substrate}\}$ . The constancy of  $k_D/k_H$  is particularly remarkable in the  $\text{CF}_3$  addition.

Several conclusions may be drawn from inspection of table 15. It is obvious that all the  $k_D/k_H$ 's are only slightly larger than unity and substantially lower than the calculated value of 1.84 expected for the tetrahedral configuration. This, we believe, indicates that the incipient R-C bond is relatively long in the transition state and that the remaining groups around the reactive center retain their original planar configuration. This conclusion is supported by the fact that the  $k_D/k_H$  seems to be unaffected by the reactivity of the substrate, and that similar values were found for  $k_D/k_H$  of the  $\text{CH}_3$  and  $\text{CF}_3$  radical addition.

Closer examination of the data seems to indicate that  $k_D/k_H$  for  $\text{CF}_3$  is perhaps slightly lower than  $k_D/k_H$  for  $\text{CH}_3$  ( $\text{C}_2\text{D}_4$  being an exception). The difference is very small, and may not be significant, but it might indicate that the incipient  $\text{CF}_3\text{-C}$  bond is longer than the  $\text{CH}_3\text{-C}$  bond.

This is a plausible conclusion, since the operation of charge-transfer forces in the reaction of the electrophilic  $\text{CF}_3$  radical are expected to reduce the repulsion forces and lengthen the incipient  $\text{C}-\text{CF}_3$  bond.<sup>3</sup>

The replacement of a hydrogen by deuterium on the carbon atom adjacent to the reactive center seems to be of little importance in the rate of the addition. This carbon atom becomes the seat of an odd electron in the eventually formed adduct radical. The  $k_D/k_H$  for  $\text{CD}_3\cdot\text{CH}:\text{CD}_2$  and  $\text{CD}_3\cdot\text{CD}:\text{CD}_2$  are 1.12 and 1.17 for the  $\text{CH}_3$  addition and 1.07 and 1.09 for the  $\text{CF}_3$  addition. However, we do not think that these small increases are significant, since the  $k_D/k_H$  values for  $\text{CD}_2:\text{CD}_2$  are 1.05 and 1.07 respectively; i.e., they are not greater than those observed for  $\text{CH}_3\cdot\text{CH}:\text{CD}_2$ .

In a recent Note, Wolfsberg and his co-workers,<sup>11</sup> criticized Streitwieser's approach to the secondary deuterium effect. They deduced from the general equation of Bigeleisen that the values of  $k_D/k_H$  do not determine the configuration of the transition state, i.e., the same  $k_D/k_H$  values may be derived whether the transition state be planar or tetrahedral. Wolfsberg's argument is not applicable to our case. It is important for the reverse reaction, namely  $\cdot\text{A}\cdot\text{CH}_3 \rightarrow \text{A} + \text{CH}_3\cdot$ . It could also invalidate a hypothetical conclusion that the transition state is tetrahedral if the  $k_D/k_H$  value were found to be high ( $\sim 1.8$ ), since then one could argue that the  $\text{R}-\text{C}-\text{H}$  bending vibration would be affected even for a planar configuration by the mere vicinity of R. However, the low values of  $k_D/k_H$ , found in our studies, are only consistent with the model in which the incipient  $\text{R}-\text{C}$  bond is relatively long and the configuration around the reactive center remains unaltered, i.e., planar.

In a recent Note by Takahasi and Cvetanovic,<sup>12</sup> published after completion of this manuscript, it was shown that  $k_D/k_H$  for the addition of H atoms to perdeutero-propylene and propylene is 1.08 at 25°C. This is an additional evidence for the planarity of the transition state.



Table 14

$k_2$  - rate constant of the addition reaction  $R \cdot + A \rightarrow RA \cdot$

$k_1$  - rate constant of the reaction  $R \cdot + \text{iso-octane} \rightarrow RH + \text{iso-octyl radical}$

Solvent - iso-octane;  $T = 65^\circ\text{C}$ , radicals produced by photolysis  
of azo-compounds  $R.N:N.R$ .  $[R.N:N.R] \approx 10^{-3}M$ .

Addition of  $\text{CH}_3$  radicals

Substrate	mole% of substrate	m.l6/m.28	$k_2/k_1$
-	0	0.5418	-
-	0	0.5420	-
$\text{CH}_2:\text{CH}_2$	2.72	0.2662	38.2
$\text{CH}_2:\text{CH}_2$	2.72	0.2635	39.0
$\text{CH}_2:\text{CH}_2$	2.72	0.2673	38.9
		Average	<u><math>38.35 \pm 0.4</math></u>
$\text{CD}_2:\text{CD}_2$	2.72	0.2586	40.4
$\text{CD}_2:\text{CD}_2$	2.72	0.2588	40.4
$\text{CD}_2:\text{CD}_2$	2.72	0.2594	40.2
		Average	<u><math>40.34 \pm 0.2</math></u>
-	0	1.653	-
-	0	1.628	-
$\text{CH}_3.\text{CH}:\text{CH}_2$	2.72	1.017	22.6
$\text{CH}_3.\text{CH}:\text{CH}_2$	2.72	1.010	23.0
$\text{CH}_3.\text{CH}:\text{CH}_2$	2.72	1.014	22.8
		Average	<u><math>22.81 \pm 0.2</math></u>
$\text{CH}_3.\text{CH}:\text{CD}_2$	2.72	0.970	25.5
$\text{CH}_3.\text{CH}:\text{CD}_2$	2.72	0.969	25.5
		Average	<u><math>25.51 \pm 0.2</math></u>
$\text{CD}_3.\text{CD}:\text{CD}_2$	2.72	0.950	26.8
$\text{CD}_3.\text{CD}:\text{CD}_2$	2.72	0.947	27.0
$\text{CD}_3.\text{CD}:\text{CD}_2$	2.72	0.960	26.1
		Average	<u><math>26.66 \pm 0.3</math></u>
-	0	0.4542	-
-	0	0.4554	-
$\text{CH}_2:\text{CH}.\text{CH}:\text{CH}_2$	0.0378	0.2540	1632
$\text{CH}_2:\text{CH}.\text{CH}:\text{CH}_2$	0.0378	0.2535	1640
$\text{CH}_2:\text{CH}.\text{CH}:\text{CH}_2$	0.0378	0.2538	1635
		Average	<u><math>1637 \pm 3</math></u>
$\text{CD}_2:\text{CD}.\text{CD}:\text{CD}_2$	0.0378	0.2321	1981
$\text{CD}_2:\text{CD}.\text{CD}:\text{CD}_2$	0.0378	0.2332	1962
		Average	<u><math>1971 \pm 8</math></u>

(Continued)

Table 14 (Continued)

Addition of CF<sub>3</sub> radicals

Substrate	mole% of substrate	(CF <sub>3</sub> H/N <sub>2</sub> )*	k <sub>2</sub> /k <sub>1</sub>
-	0	0.4615	-
-	0	0.457	-
CH <sub>2</sub> :CH <sub>2</sub>	0.0735	0.349	420
CH <sub>2</sub> :CH <sub>2</sub>	0.151	0.278	427
CH <sub>2</sub> :CH <sub>2</sub>	0.204	0.249	412
CH <sub>2</sub> :CH <sub>2</sub>	0.259	0.219	421
CH <sub>2</sub> :CH <sub>2</sub>	0.324	0.194	420
		Average	<u>420±6</u>
CD <sub>2</sub> :CD <sub>2</sub>	0.0735	0.344	447
CD <sub>2</sub> :CD <sub>2</sub>	0.152	0.272	452
CD <sub>2</sub> :CD <sub>2</sub>	0.208	0.239	441
CD <sub>2</sub> :CD <sub>2</sub>	0.263	0.208	453
CD <sub>2</sub> :CD <sub>2</sub>	0.328	0.184	455
		Average	<u>450±6</u>
-	0	0.427	-
-	0	0.421	-
CH <sub>3</sub> .CH:CH <sub>2</sub>	0.0720	0.293	621
CH <sub>3</sub> .CH:CH <sub>2</sub>	0.149	0.218	636
CH <sub>3</sub> .CH:CH <sub>2</sub>	0.200	0.184	650
		Average	<u>636±14</u>
CH <sub>3</sub> .CH:CD <sub>2</sub>	0.0723	0.285	676
CH <sub>3</sub> .CH:CD <sub>2</sub>	0.149	0.210	683
CH <sub>3</sub> .CH:CD <sub>2</sub>	0.200	0.178	688
		Average	<u>683±6</u>
CD <sub>3</sub> .CD:CD <sub>2</sub>	0.0723	0.284	686
CD <sub>3</sub> .CD:CD <sub>2</sub>	0.149	0.208	699
CD <sub>3</sub> .CD:CD <sub>2</sub>	0.200	0.178	688
		Average	<u>691±7</u>
-	0	0.450	-
-	0	0.451	-
-	0	0.452	-
CH <sub>2</sub> :CH.CH:CH <sub>2</sub>	0.916.10 <sup>-2</sup>	0.308	5043
CH <sub>2</sub> :CH.CH:CH <sub>2</sub>	1.89.10 <sup>-2</sup>	0.230	5079
CH <sub>2</sub> :CH.CH:CH <sub>2</sub>	2.54.10 <sup>-2</sup>	0.202	4860
CH <sub>2</sub> :CH.CH:CH <sub>2</sub>	3.23.10 <sup>-2</sup>	0.166	5314
CH <sub>2</sub> :CH.CH:CH <sub>2</sub>	4.04.10 <sup>-2</sup>	0.142	5390
		Average	<u>5137±215</u>

(Continued)

Table 14 (Continued)

Addition of CF<sub>3</sub> radicals

Substrate	mole% of substrate	(CF <sub>3</sub> H/N <sub>2</sub> )*	k <sub>2</sub> /k <sub>1</sub>
CD <sub>2</sub> :CD <sub>2</sub> :CD <sub>2</sub>	0.96.10 <sup>-2</sup>	0.297	5373
CD <sub>2</sub> :CD <sub>2</sub> :CD <sub>2</sub>	1.77.10 <sup>-2</sup>	0.215	5583
CD <sub>2</sub> :CD <sub>2</sub> :CD <sub>2</sub>	2.69.10 <sup>-2</sup>	0.176	5798
CD <sub>2</sub> :CD <sub>2</sub> :CD <sub>2</sub>	3.41.10 <sup>-2</sup>	0.156	5539
CD <sub>2</sub> :CD <sub>2</sub> :CD <sub>2</sub>	4.25.10 <sup>-2</sup>	0.130	5783
Average <u>5615±180</u>			
-	0	0.449	-
-	0	0.451	-
-	0	0.453	-
Ph.CH:CH <sub>2</sub>	0.0149	0.340	2192
Ph.CH:CH <sub>2</sub>	0.0298	0.280	2058
Ph.CH:CH <sub>2</sub>	0.0446	0.231	2131
Ph.CH:CH <sub>2</sub>	0.0595	0.202	2069
Ph.CH:CH <sub>2</sub>	0.0749	0.170	2223
Average <u>2135±75</u>			
Ph.CD:CD <sub>2</sub>	0.0132	0.342	2451
Ph.CD:CD <sub>2</sub>	0.0262	0.281	2325
Ph.CD:CD <sub>2</sub>	0.0392	0.236	2319
Ph.CD:CD <sub>2</sub>	0.0524	0.203	2334
Ph.CD:CD <sub>2</sub>	0.0655	0.180	2301
Average <u>2346±60</u>			

\* (CF<sub>3</sub>H/N<sub>2</sub>) is given in arbitrary units (ratio of the peaks in the chromatogram).

Table 15Secondary deuterium effect in CH<sub>3</sub> and CF<sub>3</sub> addition reaction

Substrate	k <sub>2</sub> /k <sub>1</sub> (CH <sub>3</sub> )	k <sub>2</sub> /k <sub>1</sub> (CF <sub>3</sub> )	k <sub>D</sub> /k <sub>H</sub> (CH <sub>3</sub> )	k <sub>D</sub> /k <sub>H</sub> (CF <sub>3</sub> )
CD <sub>2</sub> :CD <sub>2</sub>	40.3	450±6	1.05	1.07
CH <sub>3</sub> .CH:CD <sub>2</sub>	25.5	682±6	1.12	1.07
CD <sub>3</sub> .CD:CD <sub>2</sub>	26.6	693±7	1.16	1.09
Ph.CD:CD <sub>2</sub>	1208	2346±60	1.11*	1.10
CD <sub>2</sub> :CD <sub>2</sub> :CD <sub>2</sub>	1971	5615±180	1.20	1.09

\* This value was taken from ref. 8.

### References for Part 3

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( over )

Rate constants  $k_2I/k_1$  and  $k_2 Br/k_1$  were found to be  $45$  and  $3 \times 10^{-3}$  respectively,  $k_1$  being the rate constant of the reaction  $PhCH_2 + \cdot CH_3 \rightarrow PhCH_2\cdot + CH_4$ . The values of  $k_2I/k_1$  and  $k_2 Br/k_1$  are compared with  $k_2H/k_1$ .

The activation energies difference  $E_2I - E_1$  was determined as  $-1.8$  Kcal/mole for the temperature range  $55-85^\circ C$ .

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4. Deuterium Effect

in  $CH_3$  and  $CF_3$

Reactions

5. Photolysis

I. AFSC Project 7367.

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